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SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

Technology Demonstration Summary

The Carver-Greenfield Process Dehydro-Tech Corporation

A demonstration of the Carver-Greenfield Process® for extracting solvents and separating components of wastes has been evaluated under the Superfund Innovative Technology Evaluation (SITE) program.

Tests were conducted in August 1991 at EPA's research facility in Edison, NJ, with the use of 650 lb of drilling-mud waste from the PAB Oil site in Abbeville, LA. The waste feed contained indigenous oil (oil-soluble organic contaminants), drilling solids, and water. The process effectively separated the waste feed into its constituent solid, aqueous and organic fractions. This summary includes a brief description of the technology, an overview of the demonstration, analytical results, and conclusions.

This summary was developed by EPA's Risk Reduction Engineering Laboratory in Cincinnati, OH, to announce the key findings of the Carver-Greenfield Process SITE demonstration that is fully documented in two separate reports (see ordering information at back).

Introduction

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency (EPA) established a formal program to accelerate the development, demonstration, and use of new or innovative technologies that offer permanent, long-term cleanup solutions at Superfund sites. This SITE program is administered by the Office of Research and Development (ORD) and the Office of Solid Waste and Emergency Response (OSWER).

The major objectives of the SITE program are to develop reliable performance and cost information. One of the selected technologies was the Carver-Greenfield (C-G) Process, developed by Dehydro-Tech Corporation (DTC).

During the demonstration, waste feed from the PAB Oil site was processed using Isopar-L, a food-grade hydrocarbon with a boiling point of about 400°F, as the solvent. Approximately 10 lb of solvent per pound of waste solids were used for each of three extractions during the two runs in the demonstration. The final solids product was determined to be nonhazardous, based on extraction by the toxicity char-

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acteristic leaching procedure (TCLP) and chemical analysis of the extract.

Process Description

The C-G Process, shown in Figure 1, separates wastes into three product streams: clean dry solids; a water product substantially free of solids and organics; and indigenous oil (a concentrated mixture of extracted organics). The process incorporates several unit operations. In the first, the prepared feedstock is slurried with a hydrocarbon-based solvent (often called "carrier oil") to fluidize the waste and to extract soluble organic materials from the solids into the solvent phase. These are typically synthetic organics, petroleum-based hydrocarbons, or other organic materials that may contaminate the solid matrix — often called the "indigenous" oil. The slurry is also dewatered in an evaporation step, yielding a water fraction. The solids are separated from the slurry by centrifugation (or other means in some applications). Multiple solvent extractions may be performed before final centrifugation. Residual solvent is then removed from the centrifuged solids by a combined hydrocarbon evaporation and stripping operation, to yield a dry, clean solids product. In the final step, the spent solvent undergoes fractional distillation to separate the extracted lighter and heavier organic components from the solvent. The recovered solvent is recycled to the fluidization operation, and the extracted "indigenous" organic fractions are disposed of.

Several factors affect the C-G Process's performance in treating waste. Important among them are the size distribution of the feed solids, oil-soluble content, water content, operating parameters, and solvent selection. These criteria, as applied to the SITE demonstration of the C-G Process, are discussed below:

Solids Size Distribution: The maximum size of the solids fed to the process is restricted to 1/4 in. To meet this requirement, the PAB Oil site waste was passed through a 1/4-in. screen during excavation and again before fluidization in the mobile pilot plant.

Oil-Soluble Content: The C-G Process can treat soils, wastes, and sludges with oil-soluble contents from parts per million (ppm) levels to levels of 75% and higher. Feeds with higher oil contents may benefit from pretreatment to remove free oils if they are present. The PAB Oil site waste contained 7% to 18% oil and did not require pretreatment.

Water Content: Waste streams with up to 99% water can be successfully treated with the C-G Process. Pretreatment (such as gravity separation) to remove free water in high-water-content wastes may be beneficial to reduce the energy costs of the process. The PAB Oil site waste contained 20% to 35% water and did not require pretreatment.

Operating Parameters: Operating parameters (e.g., temperatures, pressures, number of extractions, etc.) for the C-G Process are set according to the waste characteristics and product quality requirements. For the demonstration, these parameters were determined from bench-scale treatability evaluations and process modifications during the demonstration using the PAB Oil site waste.

Solvent Selection: The choice of solvent is generally governed by the impurities in the waste and the processing objectives. Isopar-L, a food grade oil having a boiling point around 400°F and consisting predominantly of C_{11} to C_{13} iso-paraffinic hydrocarbons, was DTC's choice for the demonstration.

The primary objectives of the C-G Process SITE demonstration included the following:

- Assess the ability of the process to effectively separate petroleum-based hydrocarbon-contaminated soils into their constituent solids, oil, and water fractions.
- Evaluate the system's reliability in treating petroleum-based hydrocarbon-contaminated soils.
- Develop capital and operating costs for the C-G Process technology that can be readily used in the Superfund decision-making process.

Secondary objectives were also defined:

- Characterize residuals (water, oil, vapor, and solids) relative to applicable standards for final disposal or further treatment.
- Document the important operating conditions of the C-G Process for application to hazardous waste sites.

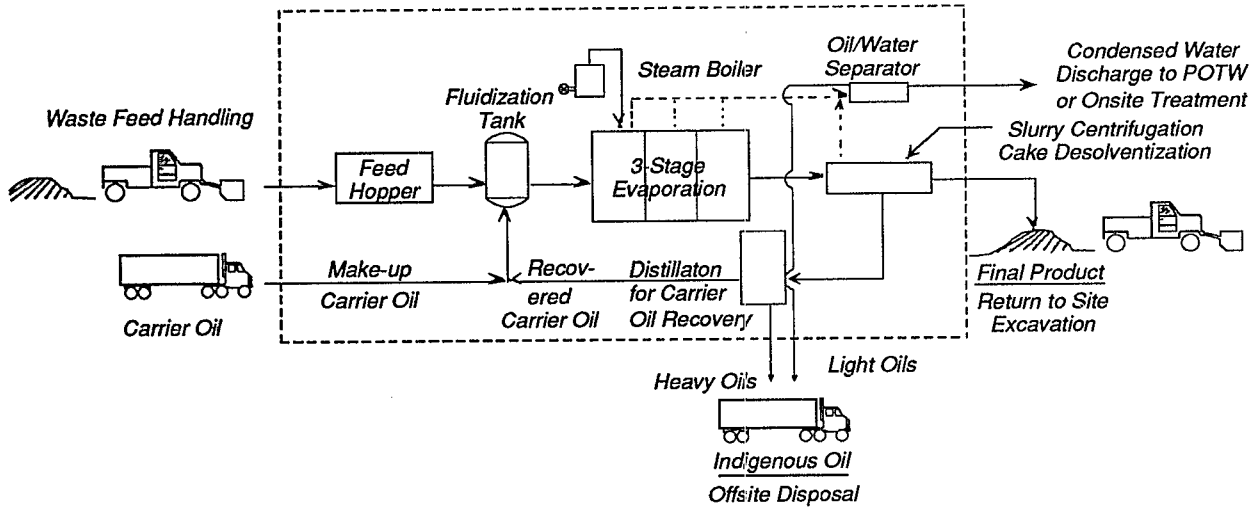

Figure 1. Simplified diagram of site remediation by the Carver-Greenfield Process.

- Assess the fate and movement of volatile and semivolatile organic contaminants and metals in the waste.

Overview of the Carver-Greenfield Process SITE Demonstration

The demonstration test runs included (1) a series of trial runs to establish optimal operating conditions, (2) a blank run, and (3) two test runs. The pilot plant was operated in a batch mode, treating approximately 300 lb of "oily" solids per test run.

The cleaned solids were tested by the TCLP test for compliance with relevant Toxicity Characteristic Rule land application limits, and for indigenous total petroleum hydrocarbons (TPH) to meet a residual target level of 0.3% (3 g/kg). The water fraction analysis conformed with specific categorical standards for organics and metals and conventional pollutant parameters relevant to conventional wastewater treatment applications.

The operating data collected included temperature, pressure, and flow measurements throughout the process. The evaporative extraction operated at 200 to 250°F, under 22 to 23 in. Hg vacuum, to ensure complete removal of water from the waste. The two subsequent extractions operated at atmospheric pressure and temperatures of 130 to 180°F. The desolventizer temperature was also important, since the desolventizer is the last point at which residual solvent and water can be removed from the solids. The desolventizer temperatures were slightly below the original projections of 225 to 350°F, which may have contributed to slightly higher than projected solvent concentrations on the final product solids.

Demonstration Results

During the demonstration, a comprehensive sampling and analysis program was undertaken to characterize the waste feed and products from the process. Solids, oil, water, and solvent analyses were interpreted to evaluate the process with respect to the primary demonstration objectives. Metals, volatile organic compounds (VOCs), and semivolatile organic compounds (SVOCs) were analyzed to qualitatively determine the fate of these materials through the process.

Sampling and Analytical Results

The sampling and analysis program focused on characterizing the following:

- feedstock;
- final product (dry solids), including TCLP results;
- recovered oils (centrate and condensed oils); and
- water product.

Each of these items is discussed below.

Feedstock Characteristics

Soil, oil, and water (SOW); TPH; solvent; VOC; SVOC; and metals were analyzed. The principal waste characterization, with respect to the primary demonstration objectives, was with the SOW analyses, which are summarized in Table 1. The two feedstocks were similar in solids content but differed in oil and water content. Both feedstocks were considered suitable for the C-G Process.

In the feedstock for Test Run 1, xylene was the only organic compound (VOC or SVOC) found above detection limits. Toluene and ethylbenzene (VOCs), and phenanthrene and 2-methyl naphthalene (SVOCs), may also have been present at concentrations less than detection limits.

In the feedstock for Test Run 2, only ethylbenzene and toluene were above detection limits. Benzene (VOC) and phenanthrene, 2-methyl naphthalene, and naphthalene (SVOC), may also have been present at concentrations less than detection limits.

The most significant metals in both feedstocks were aluminum, barium, calcium, iron, and magnesium. TPH levels ranged from 80,000 to 150,000 mg/kg; this confirmed the oil levels indicated by the SOW results. The feedstocks had no detectable Isopar-L and had ignitability levels greater than 100°C.

Final Solids Product Characteristics

The final solids product was a dry powder similar to bentonite in appearance. Isopar-L comprised the bulk of the hydrocarbon content in the final solids product. Indigenous TPH levels in the final solids product of Test Runs 1 and 2 were in trace amounts. Indigenous TPH removal efficiency is a calculated value (initial feed TPH minus final product TPH minus final product Isopar-L divided by initial feed TPH) that indicates the C-G Process's oil removal efficiency. Table 2 summarizes removal efficiencies for indigenous oil, TPH, and indigenous TPH observed in the demonstration.

TCLP analysis of the final solids product of Test Runs 1 and 2 indicated that treated solids do not leach metals, VOCs, or SVOCs above RCRA regulatory limits.

Recovered Oils Characteristics

Centrate produced in both test runs was a dark liquid with a strong odor. As expected, analyses showed relatively higher indigenous oil levels in the first extraction centrate in both test runs. The first extraction centrate contained about 87% to 89% Isopar-L, and the second and third had

Table 1. *Composition of Waste Feeds*

Test Run No.	Solids (%)	Oil (%)	Water (%)
1	52.35	17.47	21.75
2	52.44	7.26	34.7

Table 2. *Indigenous Oil and TPH Removals*

	Oil Removal Efficiency (%)		
Test Run No.	Indigenous Oil	TPH	Indigenous TPH
1	91.8	94.6	>99.9
2	88.3	92.6	>99.9

Table 3. *Oil Removal Efficiency of Extractions*

	Test 1		Test 2	
Sample Location	Indigenous Oil/Solid (g/g)	Fraction of Total Indigenous Oil Removed (%)	Indigenous Oil/Solid (g/g)	Fraction of Total Indigenous Oil Removed (%)
Feedstock	0.334	—	0.138	—
Extraction A	0.084	78.1	0.053	65.9
Extraction B	0.043	12.8	0.020	25.6
Extraction C	0.037	1.88	0.016	3.1
Final Product	0.014	7.29	0.009	5.4

levels above 98%. Table 3 summarizes the oil removal efficiency of each extraction through desolventization to the final product.

The condensed solvent product was a clear liquid in both test runs. VOCs and SVOCs were not analyzed because of elevated detection limits in the solvent matrix. Metals analyses indicated that most metals were below detection limits. The condensed solvent can be recycled in the C-G Process.

Because of scheduling constraints and equipment limitations, the final distillation step to demonstrate the separation of solvent from the indigenous oil was canceled. Therefore, the characteristics of the final indigenous oil product and solvent produced after distillation were not determined. The centrate should, however, be easily split by fractional distillation to its constituent heavy oil and solvent components; this would allow cost-effective recycling of the recovered solvent and more efficient disposal of the indigenous oil fraction.

Water Product Characteristics

The water product produced in Test Runs 1 and 2 was a clear liquid with a strong odor, low suspended solids, low biochemical oxygen demand (BOD), and high chemical oxygen demand (COD). TPH analysis results correlated well with the COD analysis results in both test runs to suggest that most of the COD was related to the presence of Isopar-L and lighter organics in the water product. Acetone and 2-butanone were detected at trace levels. No other VOCs or SVOCs were detected. Metals analyses also showed only trace amounts. The characteristics of the water product were similar to dilute municipal wastewater. The water complied with Organic Chemical, Plastics, and Synthetic Fibers (OCPSF) industrial categorical discharge limits with respect to metals and organics concentrations.

Carver-Greenfield Process Operational Reliability and Treatment Costs

The estimated cost per ton for treating drilling-mud waste from the PAB Oil site, using a full-scale C-G Process system, is about $523 per wet ton. Of this total, $221 is C-G Process technology-specific and $302 is site-specific. Of the $302 per ton site-specific cost, about $240 is for the incineration of indigenous oil separated from the feed. The estimated costs of the C-G Process are highly site-specific and difficult to identify without accurate data from a site remedial investigation report or waste profile. Variability in the waste characteristics could significantly affect treatment costs. A more detailed discussion of this technology, including a detailed discussion of economics by the vendor, is presented in the Applications Analysis Report (AAR).

Comments

This section is intended to put the demonstration results in perspective with respect to an actual full-scale site remediation. The batch-operated pilot-plant process used in the demonstration differs from an actual full-scale process unit that would be used in a site remediation.

Bench-scale and possibly pilot-scale treatability studies should be done with the actual waste material to aid in solvent selection and to identify critical operating parameters and extraction-evaporation sequence. These studies should simulate continuous or semi-continuous operations and should incorporate any special start-up conditions that a full-scale system might require.

The age and condition of the C-G Process pilot-plant equipment somewhat compromised the efficiency of two critical unit operations in the demonstration. The condition of the centrifuge required that the slurry be double centrifuged after the last extraction before the final desolventization. The desolventizer malfunctioned before the blank run; although operable during the demonstration, it ran at a lower temperature than originally planned. This may have resulted in solvent levels on the final product that were slightly elevated over initial projections.

Gross material balances were done on the blank run and the test runs to determine the integrity of the analytical results and weight measurements. More than 5,500 lb of materials, including solvent, were charged to the system in each test run; more than 96% were recovered. On a constituent basis, 80% of the solids, 107% of the water, and 96% of the oil phases charged to the system were recovered in Test Run 1. Similarly, 79% of the solids, 95% of the water, and 93% of the oil phases charged to the system were recovered in Test Run 2. The gross material balance results suggest that the measurement techniques and analytical methods sufficiently characterized the movement of materials through the process.

Conclusions

Based on the SITE demonstration results, the following conclusions can be made concerning the C-G Process:

1) The C-G Process separated a petroleum-oil-contaminated waste drilling mud into its solids, oil, and water phases. The C-G Process removed about 90% of the indigenous oil (as measured by the SOW procedure). No detectable levels of indigenous TPHs were found on the final solids product from either test run.
2) The final solids product was a dry powder similar in character to dry bentonite. Isopar-L solvent, a food grade oil, comprised the bulk of the residual oil content on the final solids product.
3) Values for all metals and organics were well below the RCRA TCLP limits for characteristic hazardous wastes. Residues from the C-G Process may still require disposal as hazardous materials because of the regulatory constraints governing the disposal of Superfund wastes.
4) The C-G Process, as demonstrated on the PAB Oil site wastes, does not remove metals bound to the solids phase. The process may increase the apparent metals concentration in the solids fraction by volume reduction.
5) The resulting water product requires further treatment because of light organics and solvent. In some cases, the wastewater may be disposed of at a local publicly owned treatment works.
6) A full-scale C-G Process system can process drilling-mud waste from the PAB Oil site at an estimated cost of $523 per wet ton of feed. Of this total, $221 is C-G Process technology-specific and $302 is site-specific. Of the $302 per ton site-specific cost, about $240 is for the incineration of indigenous oil separated from the feed. Treatment costs are highly site-specific, and accurate cost estimation requires data from a site remedial investigation or waste profile, as well as specific treatment goals. Variability in the waste characteristics or pretreatment requirements could significantly affect treatment costs.

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The complete report, entitled "Technology Evaluation Report: The Carver-Greenfield Process, Dehydro-Tech Corporation," (Order No. PB92-217462AS; Cost: $35.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Applications Analysis Report: The Carver-Greenfield Process, Dehydro-Tech Corporation" (EPA/540/AR-92/002) is available.

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